NASA Exobiology Program Final Report, NAG5-11488
Spectroscopic Studies of Pre-Biotic Carbon Chemistry
Performance Period 3/01/02-2/28/03

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I. Final Report for Exobiology FY02 Funding

As described in the original proposal and in our progress reports for NAG5-8822, research in the Blake group supported by the Exobiology program seeks to understand the pre-biotic chemistry of carbon along with that of other first- and second-row elements from the earliest stages of star formation through the development of planetary systems. The major tool used is spectroscopy, and the program has observational, laboratory, and theoretical components. The observational and theoretical programs are concerned primarily with a quantitative assessment of the chemical budgets of the biogenic elements in the circumstellar envrionment of forming stars and planetary systems, while the laboratory work is focused on the complex species that characterize the pre-biotic chemistry of carbon. We outline below our results over the past year acquired, in part, with Exobiology support.

Observational Characterizations of Pre-Biotic Chemistry

We continue to employ both Caltech and international facilities in our telescopic studies of pre-biotic chemistry in the circumstellar accretion disks around young stars and in the comae of comets. This part of the Exobiology effort combines observations of young stellar systems at the best spatial resolution achievable, detailed radiative transfer and chemical modeling, and laboratory/spacecraft measurements of grain/grain mantle properties to study protostellar, and potentially protoplanetary, nebulae. Our major work in preparation for the start of the new grant is to get ready for the launch of SIRTF and to acquire the necessary laboratory spectra to guide astronomical searches for complex molecules.

During this one year completion of our ongoing Exobiology grant, we have completed detailed modeling studies on the morphology and chemistry of individual YSOs. As noted previously, students supported by our current and previous Exobiology grants have been involved in making some of the first sub-arcsecond resolution observations with the OVRO array, in continuing our chemical studies of individual systems, in the analysis of mid- and far-infrared spectra taken by ISO, and in continuing exploratory near- and mid-infrared diffraction limited imaging and spectroscopy at the Keck telescopes.

Notable recent accomplishments, described in more detail below, include:

- ◇ optimizing detailed radiative transfer modeling of the molecular and dust emission from YSO envelopes and from comets, including a new parallelized implementation,
- ◇ modeling chemical zonation in the outer regions of T Tauri star accretion disks, particularly fractional ionization and D/H studies,
- ◇ acquiring and modeling the first CO $v = 1 \rightarrow 0$ emission spectra from the terrestrial planet-forming region of circumstellar accretion disks.

Chemistry in Disks and the Connections to Comets

To date, most spectral line imaging of disks around T Tauri (TTs) and Herbig Ae (HAe) stars has been carried out in isotopomers of CO for reasons of sensitivity (e.g. Dutrey et al. 1994; Koerner & Sargent 1995; Mannings & Sargent 1997). With support from this program we have pioneered studies of the chemical properties of circumstellar disks – properties of great importance to Exobiology. For example, we have imaged the emission from more complex species such as HCO^+, HCN, and H_2CO interferometrically (see also related single dish work by Dutrey et al. 1997, Kastner et al. 1997). These important first data suggest that chemical studies can now be profitably pursued in at least some disks.

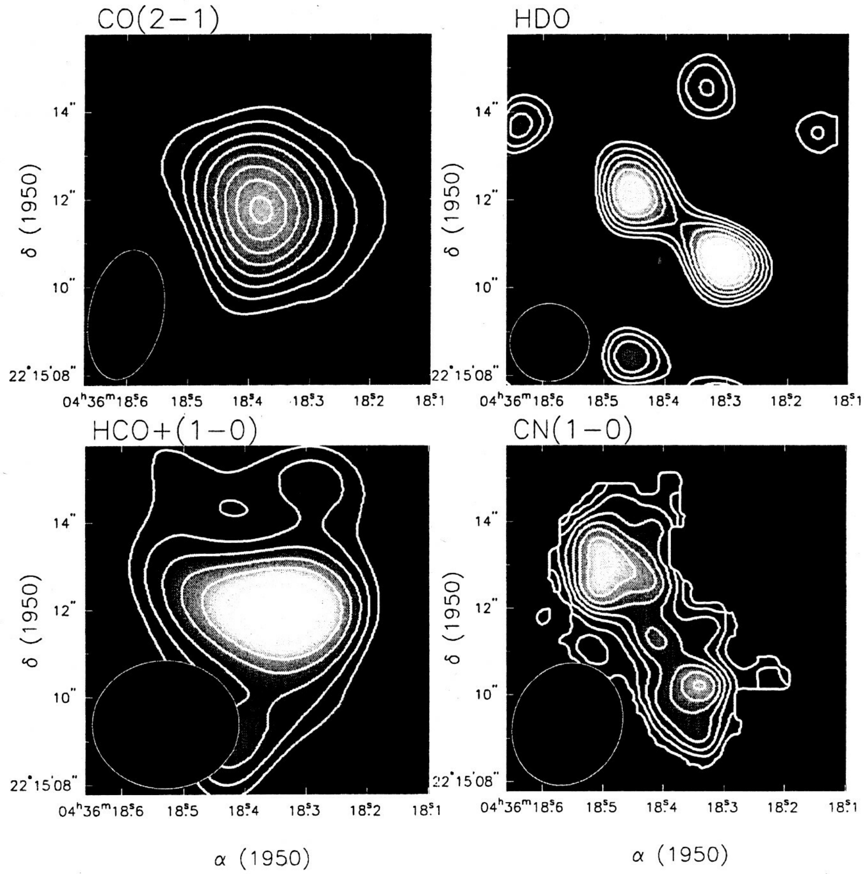

Figure 1. OVRO Millimeter Array observations of CO HDO, HCO^+ and HCN toward the T Tauri star LkCa 15. While CO and HCO^+ are centered at the stellar position, CN, HDO and HCN (not shown) peak ~2" away.

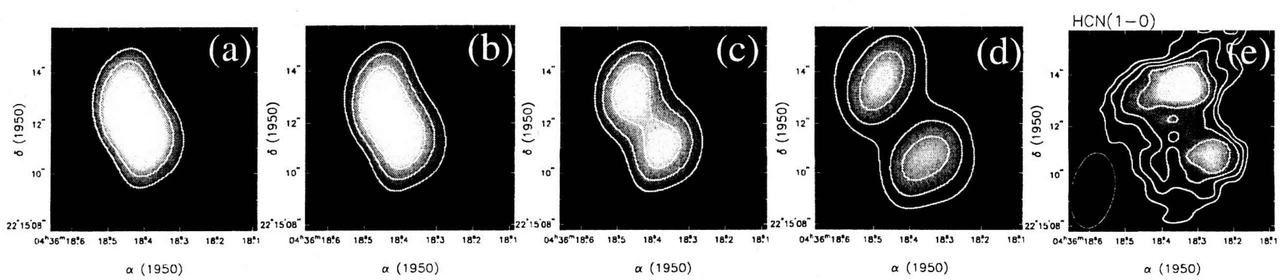

Figure 2. Model fits to the HCN J=1-0 emission from LkCa 15. The observed HCN emission (e) is compared to a model of an anulus of HCN with an outer radius of 400 AU and an inner radius of 50 (a), 100 (b), 200 (c) and 300 AU (d). In each case, the total flux of the model image is set to match the observed' HCN map. The observed emission is consistent with an inner radius between 200 AU and 300 AU (between (c) and (d)).

In order to examine accretion disks in detail and to test models of disk chemistry and transport, we are continuing an intensive multi-species imaging study of two T Tauri and two Herbig Ae stars (Kessler, Ph.D. Thesis, supported in part by this grant; Qi et al. 2003, Kessler et al. 2003). The target systems are isolated from molecular clouds and have ages of at least 2 MYr. Interferometric images of several species in the C-, N-, O-, and S-bearing chemical families, including a number of isotopic variants, have been acquired. Maps of the intense CO and CN emission from the TTs LkCa 15 are shown in Figure 1. Clearly, even at the 3-5″ resolution achieved CO/CN distributions are dramatically different, and reveal enhanced CN abundances outside 200-300 AU. Both ion-molecule and photon-dominated chemistry must contribute to the observed abundances since the CN/HCN and HDO/H_2O ratios are too high to be accounted for by quiescent chemistry (Spaans 1996, Dutrey et al. 1997, Kastner et al. 1997), but can be explained by models invoking selective molecular depletion in the outermost regions of the disk (Aikawa & Herbst 1999). Interestingly, the D/H ratio, measured for the first time in the disk of LkCa 15, is very high, 0.008, and is quite similar to those measured in the cold, dense cores of molecular clouds.

These new measurements of the chemistry in the outer regions of circumstellar disks tell us about the formation and evolution of other protoplanetary nebula, and by inference about our own. On the other hand, comets, among the most pristine remnants of the early solar nebula, provide a historical record of the evolution of ices and gases in our solar system. Millimeter-wave aperture synthesis directly probes the inner coma of comets, a region suffering from obscuration and scattering problems in optical and infrared measurements, but the region containing the most pristine cometary gases. The millimeter-wave arrays can sample small-scale ($\geq 1''$) structures near the nucleus with sub-km s^{-1} velocity resolution.

For her thesis, Ms. Kessler has created a model to simulate our observed channel maps and images of protoplanetary disks. The temperature and hydrogen density distributions are determined using physically self-consistent disk models, assuming a power law distribution of dust sizes ($n(a) = a^{-3.5}$), an accretion rate of 10^{-8} $M_\odot$/yr and equal dust and gas temperatures. The resulting physical disk model is then combined with the distribution of the molecule of interest and the radiation transfer in the disk is calculated using a non-LTE Monte Carlo code (Hogerheijde & van der Tak 2001). The input parameters for this model are the mass and inclination of the disk. The inner and outer radius of the disk and turbulent velocity width (0.1 km/s) are parameters which are adjusted to fit our observed CO 2-1 emission spectra. As Figure 2 shows, the ~constant column density models that fit the CO emission well cannot reproduce the CN, HCN, or HDO distributions, which are peaked well away from the star. In each panel of Figure 2 the column density of HCN in the ring is set by matching the integrated flux of the modeled map to that observed. As we vary the inner radius we can see that these models can reproduce the structure of the HCN emission only with large depletion zones in the disk center ($R_i \sim$ 200-300 AU). More realistic models will be used in the future to simulate the combined effects of desorption from grains and photodissociation of HCN from interstellar and stellar UV.

Our first work in expoloring the comet-origins connection was on Comet C/1995 O1 (hereafter Hale-Bopp), an exceptionally large and productive long-period comet that provided an opportunity to study the physical and chemical properties of cometary material in unprecedented detail. At OVRO, emission from twelve different molecules was imaged along with the thermal emission from nucleus and its surrounding coma over a five day period in March/April 1997. The measured (D/H) ratios are similar to those seen in LkCa 15 and further suggest that Hale-Bopp, and by inference the outer solar nebula in general, consists of ~15-40% largely unprocessed interstellar material (Blake et al. 1998). The discrepancy between the comet D/H ratios and that of the earth's oceans likely eliminates long period comets as the major source of water on earth (c.f. Meier et al. 1998).

These millimeter-wave studies are well suited to examining the outermost reaches of

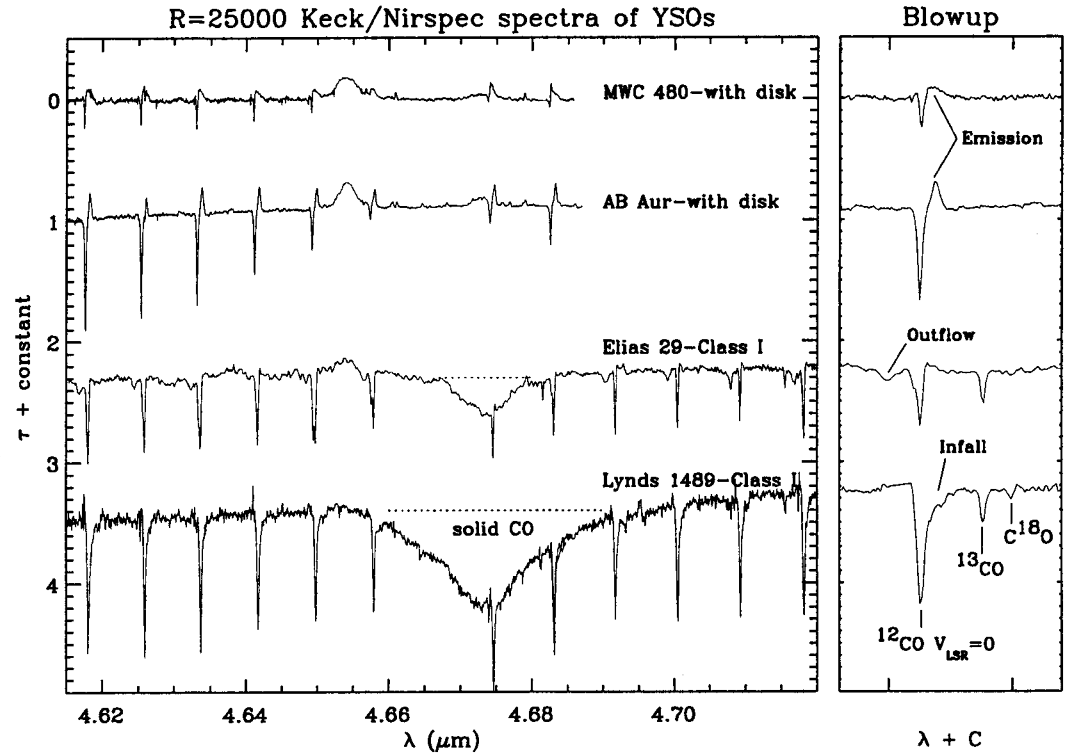

Figure 3. Keck NIRSPEC spectroscopy of the 4.67 μm CO fundamental vibration toward low mass protostars at various stages of evolution. Age increases toward the top. The CO ice band visible in the youngest sources with surrounding cores or extended disks (L1489 and Elias 29) is a well established tracer of thermal processing, while the narrow absorption lines directly trace the physical conditions and velocity fields of the surrounding gas. The redshifted wings on the L1489 lines trace infalling gas to within a few stellar radii of the central object (Boogert et al. 2002a). In sources with accretion disks, CO emission becomes visible, and traces warm, dense gas in accretion flows or gaps in the terrestrial planet-forming region. Information on the location of the emitting gas is contained in the line profiles that are clearly resolved with NIRSPEC. The absorption in AB Aur and MWC 480, whose spectra were acquired at high airmasses, is caused by the atmosphere. Measurements at different times of the year can be used to shift the astronomical and atmospheric features and clean up the spectrum (Boogert et al. 2002b).

circumstellar accretion disks and the outer reaches of the solar system, but tell us little about the terrestrial planet-forming regions of the disks around pre-main sequence stars. The discovery of extrasolar 'hot Jupiters' some 0.05 AU from their parent stars (Marcy, Cochran & Mayor 2000) has highlighted the important role of star-disk-protoplanet interactions, and demands new tools that can investigate the critical 1-10 AU planet-forming zone of disks (Lin et al. 2000, Ward & Hahn 2000, Trilling et al. 1998), The observational characterization of gaps and of the fraction of disks containing Jovian protoplanets therefore forms a pivotal counterpoint to the highly successful radial velocity extrasolar planet searches.

Only high resolution spectroscopy permits robust access to these spatial scales at present (see Najita et al. 2000). Indeed, the potential signatures are very large. Jupiter induces a stellar velocity wobble of only 13 m s^{-1}, for example, while alterations to the disk kinematics can be a large fraction of the orbital velocity of $\sim$20 km s^{-1} at 5 AU. Gas in and near the $\lesssim$AU gaps opened up by protoplanets can be heated by the star and, if the planet is massive enough, by shocks (Bryden et al. 1999, Kley 1999). The total amount of hot, dense gas is small, but it radiates strongly in the IR since it is adjacent to the low density gap. Abundant species such as H_2, H_2O, and CH_4 are excellent candidate tracers, but they are very difficult to observe from the ground.

CO is an abundant, stable molecule widely spread throughout the disk (and any envelope, if present). Mm-wave CO emission lines trace nicely the outer disk (Beckwith & Sargent 1996), while $\Delta v = 2$ overtone emission near 2.3 μm arises from the several thousand degree gas immediately adjacent to the young star (Scoville et al. 1983, Najita et al. 1996), but can only be observed in a handful of stars. CO absorption at 2.3 and 4.6 μm traces cold gas and ice with moderate optical depths, leaving *emission* from the the CO vibrational fundamental near 4.6 μm as a potential gap/protoplanet tracer. In a study of 8 spectroscopic binary systems, 5 show measurable CO $v = 1 \rightarrow 0$ emission thought to arise from a gap in the circumbinary disk, an interpretation consistent with the CO line shapes (Najita et al. 2000). For the observed intensities of $\sim$10^{-16} W m^{-2}, the total amount of radiating material is only 10^{-5} earth masses, with a T$\gtrsim$1100 K. For T$\sim$300 K, the same line strength would correspond to a mass of only $\sim$0.01 M$_\oplus$ at the distance of Taurus!

We have therefore taken a two pronged approach to the study of inner disk regions. Using the ISO satellite we have measured, for the first time, the pure rotational H_2 emission from both accretion and debris disks (Thi et al. 2001a,b). These results have accurately constrained the gas mass in disks for the first time, and have revealed that gas is present around young stars for much longer than previously believed. We have also begun a program of 4.67 μm CO observations of CO using the NIRSPEC spectrograph at the Keck II telescope. We have studied a carefully selected sample of lines of sight, ranging from quiescent dense clouds, to embedded young protostars, to more evolved, disk dominated protostars. Our initial results demonstrate the tremendous power of this tracer, as outlined in Figure 3.

The velocity widths in the emission spectra yield characteristic radii of several $\times$ 0.5-3 AU that are well correlated with, but larger than, the 2 μm sizes derived from interferometry. The measured linewidths also follow the disk inclination, with face-on systems having the narrowest velocity widths, and so it is unlikely that these lines originate in an outflow or disk wind. A range of excitation temperatures, $\sim$50-1500 K, are found even within single disks, but the bulk of the gas lies at temperatures of 500-1000 K. The total line emission is typically less than 10% of the 5 μm continuum flux. Neither the continuum nor line emission is resolved at the typical 0.″4-0.″5 seeing conditions at M-band.

These properties are consistent with the irradiation of a shadowed region of the disk *surface* by a "puffed up" ring of hot dust responsible for the near-IR continuum in these sources whose extent has been measured by K-band interferometry. The total amount of radiating material is difficult to estimate since the source is unresolved, but using the slit width ($\sim$0.″45) results in very small masses, typically $\ll$M$_\oplus$, since IR radiative pumping is very efficient at low optical depths. This same process should occur for any molecule with active vibrations, and the examination of several species would provide exceptional probes of the disk physical conditions at radii near 1 AU. Thus, results such as these herald the advent of an exciting era of discovery in which specific tracers of disk/planetary system evolution (the assembly of proto-Jovian sub-nebulae, gap formation, planet migration, etc.) can be

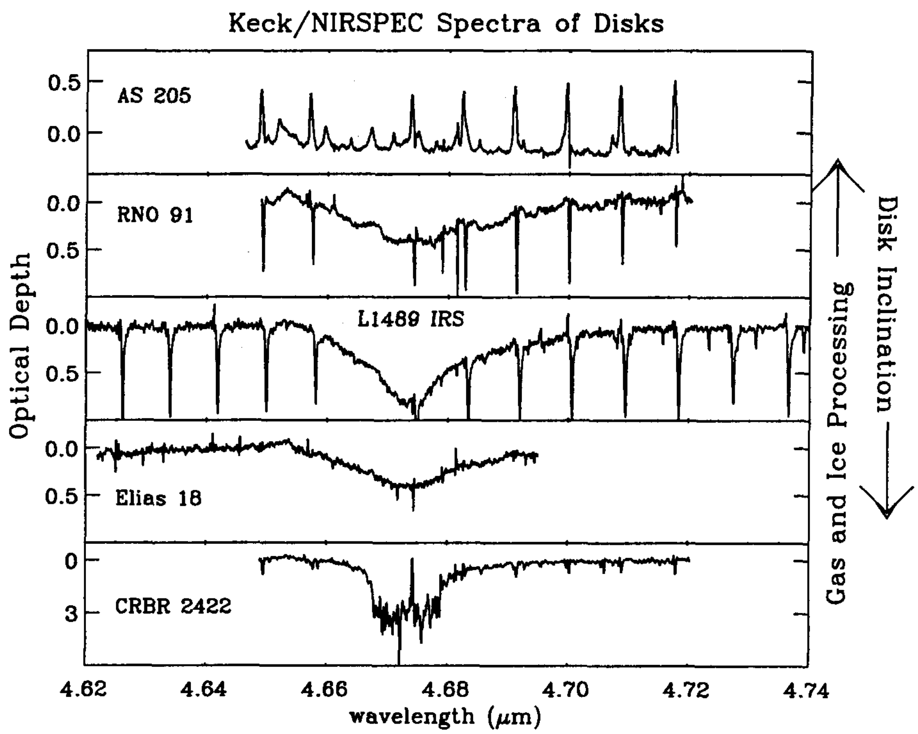

Figure 4. NIRSPEC R=25,000 CO spectra of the edge-on disks RNO91, L1489, Elias 18, and CRBR2422 on an optical depth scale; showing both gas phase and solid state features (the ice/gas ratio increases downward as successively denser regions near the disk mid-plane are probed). RNO91 shows broad emission (inner disk) and narrow absorption (outer disk), while the CO ice band in CRBR2422 is highly saturated (note the large change in the optical depth scale). Depletion estimates for this source are therefore lower limits. Finally, the rich emission line spectrum from the isolated T Tauri star AS205 is plotted at the top for comparison with the spectra observed from disk surfaces.

investigated in large samples of objects with spectroscopy. Interferometry could then be used to follow up these surveys with high spatial resolution images.

As the inclination angle of the disk with respect to the observer increases, eventually it will begin to occult the central star and the hot dust near it. Such edge-on orientations, while statistically rare, provide a unique opportunity for several reasons: (1) As Figures 4 shows, the disk can now be probed via *absorption* spectroscopy, which means that both the gas phase and solid state components of the disks can be traced. The depletion of molecules onto grains has long been suspected and is vital to planetesimal growth, but can only be directly tested via observations of edge-on disks. (2) Due to the large filling factor of the inner disk and the high column density at large radii, infrared spectroscopy of edge-on disks is sensitive to all disk regions beyond the hot dust zone. (3) Thanks to the observational geometry, the disk *radial* velocity field can be examined over a wide range of distances, as we have shown for L1489 (Boogert, Hogerheijde, & Blake 2002a). Radial mass transport is obviously a critical function of accretion disks, but only absorption spectroscopy of edge-on disks provides access to $R > 0.1$ AU at present. (4) With sufficient sensitivity, regions of the disk much closer to the mid-plane can be probed than are sampled by near-/mid-infrared emission spectroscopy.

Observations of edge-on disks at slightly different inclination angles make it possible to sample different heights within the disk; with slightly tilted disks offering access to near-surface layers and disks nearly perfectly edge-on sampling closer to the mid-plane. Molecular depletion should vary systematically with inclination angle, and as molecules deposit themselves onto grains there should be substantial changes in the gas fractional ionization. This has implications for mass transport in disks via magnetic instabilities, and so it will be essential to probe both neutral and ionic species in future observations. Of the various edge-on disks discovered over the past decade, only a handful of these can be studied even the excellent sensitivity of Keck/Gemini/VLT thanks to the large extinction provided by the disk itself.

Laboratory Studies of Complex Pre-Biotic Molecules

The Blake group relocated over the past two years to a new laboratory in the Beckman Institue, which provides substantially more space (nearly 2500 sq. feet) and clean room quality air over the optical benches. During the move and the subsequent disruption of our ability to carry out studies under UHV conditions, we have been developing important new light source capabilities that are now operational. At long wavelengths, for example, difference frequency methods produce very broad tunability compared with our existing spectrometers, including the pivotal THz region. Recent tests of difference frequency mixing in GaAs have revealed cut-off frequencies nearer to 3 THz, which will enable the rotational spectra of *all* interstellar molecules and first-row atomic fine structure transitions to be studied with sensitive SIS receivers from future platforms such as SOFIA and FIRST. Further, the vibration-rotation-torsion spectra of more complex molecules may be best studied at THz frequencies, as outlined below.

The chemistry of carbon is characterized by an extraordinary array of structures and reactivities. In the diffuse interstellar medium this extraordinarly complex chemistry is relected in our emerging understanding of cosmic dust, in which species as diverse as carbon chains and rings, fullerenes and fulleranes, and polycyclic aromatic hydrocarbons (PAHs) or their derivatives have all been proposed as carriers of the diffuse interstellar bands (DIBs) and unidentified infrared emission features (UIRs) – spectral features which are used to trace the presence of "molecular grains." In dense interstellar gas, more saturated compounds are rapidly synthesized, and recent theoretical models have suggested that truly pre-biotic species may be formed in considerable abundance (Charnley 2000).

Over the course of the last year we have been examining the millimeter-wave and THz spectra of important pre-biotic molecules with our OPO and difference frequency spectrometers in order to search for such species with the soon to be completed SOFIA and FIRST/Herschel observatories since their softest THz modes may also offer a more sensitive way to search for complex species in dense interstellar clouds. Consider the case of glycine, for example, which has long been sought after unsuccessfully at microwave and millimeter-wave frequencies (Snyder 1997). Even with the nuclear and electronic partition functions set to unity, careful considerations of the glycine vibrational manifold lead to a partition function of ~650,000 at 300 K! Calculated 0 to 3 THz spectra for the four lowest conformers of glycine (here, conformers refers to the relative orientations of the carboxylic acid and amino functional groups of glycine) show that the THz Q branches are substantially stronger (by factors of 100-1000) than the pure rotational transitions at centimeter and millimeter wavelengths at room temperature. Under low temperature conditions, the relative intensity ratios will be even more in favor of the THz bands.

We have recently installed both heated pulsed nozzles and laser desorption sources, and have created a novel "pick up" source in which two expansions are crossed to create new species that are too reactive to produce in single expansions. Our first application of this source is described in our work on sodium-water and sodium-ammonia clusters that appeared in *Chemical Physics Letters.* We have now used these sources to acquire and assign the spectra of species such asdihydroxyacetone, the second simplest sugar after glycoaldehyde, recently detected in hot cores, and amino acids.

II. Publications Since 2001 Under the Current Grant

"Substantial Reservoirs of Molecular Gas in the Debris Disks around Young Stars" Wing-Fai Thi, Geoffrey A. Blake, Ewine F. van Dishoeck, Gerd-Jan van Zadelhoff, J. Horn, E.E. Becklin, V. Mannings, A.I. Sargent, M.E. van den Ancker, & A. Natta 2001, *Nature* **409**, 60.

"Spectral Energy Distributions of Passive T Tauri and Herbig Ae/Be Disks: Grain Mineralogy, Parameter Dependences, and Comparison with ISO LWS Observations" E.I. Chiang, M.K. Joung, M.J. Creech-Eakman, C. Qi, J. Kessler, G.A. Blake, & E.F. van Dishoeck 2001, *Ap. J.* **547**, 1077.

"Chemical Evolution of Protostellar Matter" William D. Langer, Ewine F. van Dishoeck, Edward A. Bergin, Geoffrey A. Blake, Alexander G.G.M. Tielens, Thangasamy Velusamy, & Douglas B. Whittet 2001, *Protostars & Planets IV*, V.G. Mannings, A.P. Boss & S.S. Russell, eds., (Univ. Arizona, Tucson), 29-58.

"Submillimeter Lines from the Circumstellar Disks around Pre-Main Sequence Stars" Gerd-Jan van Zadelhoff, Ewine F. van Dishoeck, Wing-Fai Thi, & Geoffrey A. Blake 2001, *Astron. Ap.* **377**, 566.

"Microwave and THz Spectroscopy" Geoffrey A. Blake 2001, *Encylopedia of Chemical Physics & Physical Chemistry*, J. Moore, N. Spencer, eds. (Institute of Physics Publ., Bristol), pp. 31-44.

"ISO LWS Spectra of T Tauri and Herbig AeBe Stars in Taurus and Ophiuchus" M.J. Creech-Eakman, E.I. Chiang, Ewine F. van Dishoeck, & Geoffrey A. Blake 2002, *Astron. Ap.*, 385, 546.

"High Resolution 4.7 μm Keck/NIRSPEC Spectra of Protostars. I: Ices and Infalling Gas in the Disk of L1489 IRS" A.C.A. Boogert, M.R. Hogerheijdge, & Geoffrey A. Blake 2002, *Ap. J.* **568**, 761.

"The Environment and Nature of the Class I Protostar Elias 29: Molecular Gas Observations and the Location of Ices" A.C.A. Boogert, M.R. Hogerheijde, C. Ceccarelli, A.G.G.M. Tielens, E.F. van Dishoeck, G.A. Blake, W.B. Latter, & F. Motte 2002, *Ap. J.* **570**, 708.

"A Tidally Interacting Disk in the Young Triple System WL20?" M. Barsony, T.P. Greene, & Geoffrey A. Blake 2002, *Ap. J.(Letters)* **572**, L75.

"Looking for Pure Rotational H_2 Emission from Protoplanetary Disks" M.J. Richter, D.T. Jaffe, Geoffrey A. Blake, & J.H. Lacy 2002, *Ap. J.(Letters)* **572**, L161.

"Does IRAS 16293-2422 Have a Hot Core? Chemical Inventory and Abundance Changes in its Protostellar Environment" F. L. Schöier, J. K. Jørgensen, E. F. van Dishoeck, & Geoffrey A. Blake 2002, *Astron. Ap.* **390**, 1001.

"High Resolution 4.7 μm Keck/NIRSPEC Spectra of Protostars. II: Detection of the ^{13}CO Isotope in Icy Grain Mantles" A.C.A. Boogert, Geoffrey A. Blake, & A.G.G.M. Tielens 2002, *Ap. J.* **577**, 271.

"Millimeter-wave Searches for Cold Dust and Molecular Gas around T Tauri Stars in MBM 12" Michiel R. Hogerheijde, Ray Jayawardhana, Doug Johnstone, Geoffrey A. Blake & Jacqueline E. Kessler 2002, *Astron. J.* **124**, 3387.

"Millimeter Wavelength Measurements of the Rotational Spectrum of 2-Aminoethanol" Susanna Widicus, Brian J. Drouin, Kathryn A. Dyl, & Geoffrey A. Blake 2003, *J. Mol. Spec.* **217**, 278.

"Interferometric Observations of Formaldehyde in the Protoplanetary Disk around LkCa15" Yuri Aikawa, Munetake Momose, Wing-Fai Thi, Gerd-Jan van Zadelhoff, Chunhua Qi, Geoffrey A. Blake, & Ewine F. van Dishoeck 2003, *P.A.S.J.* **55**, 11.

"Continuum and CO/HCO+ Emission from the Disk Around the T Tauri Star LkCa 15" Chunhua Qi, Jacqueline E. Kessler, David W. Koerner, Anneila I. Sargent, & Geoffrey A. Blake 2003, *Ap. J.*, in press.

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